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Effect of preparation methods on the catalyst performance of Co/Mg–La mixed oxide catalyst for CO_x-free hydrogen production by ammonia decomposition

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ABSTRACT

This work deals with the effect of catalyst preparation method of the mixed Co, Mg and La oxide catalysts on their structure and catalytic properties for ammonia decomposition. Two methods are used for catalysts preparations impregnation and co-precipitation (in air and in pure O₂ atmosphere), The Mg/La = 2 molar ratio and 5 wt% of cobalt content was maintained same in all catalysts. The catalyst performance was evaluated in the temperature range 300–550 °C at atmospheric pressure. The prepared catalysts were characterized by BET, XRD, TPR, XPS, CO₂-TPD and SEM techniques. No pronounced differences were observed in BET among the catalysts. It was found that the 5CML-OXY (5 wt%Co over Mg–La catalyst prepared by co-precipitation method in oxygen atmosphere) has superior activity among the other catalysts. This could be attributed to availability of easily reducible cobalt species determined by TPR studies and enhanced interaction between Mg and La determined by SEM and XPS. The moderate basic site density determined by CO₂-TPD results was also increased in 5CML–OXY catalysts compared with other catalysts. These consequences are might be one of the reasons for enhanced activity of 5CML–OXY catalyst compared to other catalysts. Hence catalyst preparation by co-precipitation in oxygen atmosphere is the best method which might be one of the parameters that influenced on catalytic properties of the cobalt on MgO–La₂O₃ system, for ammonia decomposition.

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Introduction

Hydrogen is an important energy carrier, especially for fuel cells applications. However, the low volumetric density of

hydrogen even in compressed gas form makes the storage of hydrogen a difficult problem for most of the possible applications. This limitation is felt most strongly in the area of onboard storage, but it is also a problem in the delivery and distribution of hydrogen. Hydrogen's low energy density is

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perhaps one of the greatest barriers to the implementation of hydrogen in fuel cell driven vehicles [1–3]. Ammonia is a promising chemical storage media that contains hydrogen in chemically bonded form. The ammonia molecule has the largest hydrogen weight fraction of 17.65% among all known molecules. The chemically bonded hydrogen can be released by ammonia catalytic decomposition. Ammonia can be liquefied under mild conditions (the vapor pressure of ammonia at room temperature is 9.2 bars). The infrastructure for handling and transportation of bulk ammonia quantities is already well established in many countries. Liquid ammonia is readily available, because it is the second most widely produced chemical in the world with low production cost. Ammonia possesses narrow explosion limits [4]. For these reasons ammonia decomposition on metal catalysts has been extensively studied as method of very clean hydrogen production. “On-site” generation of CO_x-free hydrogen from ammonia decomposition for fuel cell applications has recently attracted much attention [1]. It has been reported that ammonia ‘on-site’ decomposition is economically more feasible process than methanol reforming for hydrogen generation especially in the case of “on board” H₂ generation [1,5].

Noble and transition metals (Ru, Ir, Pt, Rh, Fe, Ni and Co) on different supports, metal nitrides (Mo₂N, VN_x, Fe₃Mo₃N, Co₃Mo₃N and Ni₃Mo₃N) and metal carbides (MoC_x and VC_x) were tested as catalysts for ammonia decomposition reaction [4,6–21]. It was found that among all the tested catalysts, the supported Ru is the most active. However, the possibilities for wide applications of Ru are limited. The very high price and scarce availability of Ru are the major obstacles for large-scale applications of Ru catalysts. Hence it is highly attractive task to develop an active and affordable catalyst for ammonia decomposition.

Transition metals such as Fe, Co and Ni catalysts are suitable candidate for this role. Unfortunately, even at low temperatures in iron systems are forming stable nitrides, which have low catalytic activity [11]. Although Ni is less expensive than Co, nickel catalysts are showing acceptable catalytic activity only at elevated temperatures [12,22,23]. Because of these reasons, we decided to concentrate our efforts to study Co containing system.

A wide variety of supports such as Al₂O₃, SiO₂, TiO₂, ZrO₂, meso-porous and micro-porous materials, activated carbon, graphene, multi-walled carbon nanotubes (MWCNTs) have been examined as support for preparation of effective ammonia decomposition catalysts [22,24–26]. Among them MWCNTs supported catalysts have shown the highest activity.

It is well known that good catalyst support should possess a complex of suitable properties like stability at reaction conditions, high surface area and appropriate chemical characteristics. For carriers of catalysts for ammonia decomposition essential is the presence of suitable surface basicity [1]. In search for an effective support for Co catalysts we studied different basic mixed oxides. We have found that cobalt catalyst supported on Mg–La have shown very promising activity for ammonia decomposition [14,15]. We also have reported that the optimal Mg: La ratio is equal to 5. Another important finding was that calcinations of both support and catalyst in N₂ led to increased activity compared to catalysts calcined in static air condition [15].

For better understanding of the chemical characteristics of the metal-support interaction, we have studied the effect of preparation method of Co catalysts on their performance for ammonia decomposition.

Therefore, the aim of present work is to investigate the effects of preparation method of Mg–La mixed oxide supported cobalt systems on the catalytic performance for ammonia decomposition. To the best of our knowledge, the results of similar investigation have not been reported in the literature. To observe changes in activity noticeably we selected MgLa mixed oxide support with MgLa ratio equal to 2.0. The morphology, chemical, and structural characteristics of the catalysts were characterized by N₂ adsorption, XRD, TPR, XPS and SEM.

Experimental

Catalyst preparation

For preparation of Co catalysts we have used two methods impregnation and co-precipitation (in air and in pure O₂ atmosphere). The Mg, La ratio (Mg/La = 2) and the cobalt content (5 wt%) was maintained same in all catalysts.

All chemicals used in this study i.e. Mg(NO₃)₂·6H₂O, La(NO₃)₃·6H₂O, Co(NO₃)₂·6H₂O, KOH and K₂CO₃ are from Fluka with purity >99% and were used as they were supplied.

Preparation of impregnated Co/Mg–La mixed oxide (Mg/La = 2) catalyst

Mg–La mixed oxide support (Mg/La = 2) was prepared by co-precipitation from Mg and La nitrates solutions under high super saturation conditions using a mixture of KOH and K₂CO₃ [14]. In a typical synthesis of 2:1 M ratio of MgLa oxide, solution A was prepared by dissolving 0.129 mol of Mg(NO₃)₂·6H₂O and 0.0645 mol of La(NO₃)₃·9H₂O in distilled water for a 1 M solution. Solution B was prepared by dissolving 0.453 mol of KOH and 0.1225 mol of K₂CO₃ in distilled water for obtaining a 2 M solution. Then solution B was added drop wise to solution A at rate of 60 cm³ h⁻¹ under vigorous stirring at 25 °C. The precipitation continued until the pH of the liquid becomes equal to 11.0. Then the mixture was stirred for 30 min. After the base addition, the temperature of the system was increased to 70 °C and the precipitate was aged at this temperature for 18 h in static air. Then the precipitate was filtered and washed with de-ionized water until pH of washed waters becomes equal to 7.0 [14]. The obtained mixed oxide was calcined at 500 °C under N₂ flow for 15 h. For preparation of Co catalyst with 5.0 wt % loading of Co, the calcined mixed oxide was impregnated with Co from aqueous cobalt nitrate solution using a rotary evaporator. The obtained cobalt catalyst was calcined at 500 °C under N₂ flow for 15 h. This catalyst was designated as 5CML-IMP.

Preparation of Co–Mg–La co-precipitated catalyst in static air

The Co–Mg–La catalyst was prepared by means co-precipitation method. The nitrates of Co, Mg and La were dissolved in de-ionized water and the prepared metal nitrates solution was precipitated by the drop wise addition of KOH and K₂CO₃ mixture solution until pH of the liquid becomes

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